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Far infrared thermal spectroscopy of low-T_c and high-T_c superconductor films

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Temperature dependence of far-infrared transmission of NbN thin films deposited on MgO and Si substrates was measured at several frequencies from 0.4 up to 4.3 THz. Exponential increase of relative penetration depth at low temperatures and a peak in transmission near T_c was observed for frequencies below the optical gap. On the contrary, transmission measured at frequencies above the gap exhibits only flat, almost linear temperature dependence. This behavior is consistent with the BCS theory of superconductivity. Similar measurements were performed also on $YBa_2Cu_3O_{7-\delta}$ thin films deposited on MgO and sapphire substrates. Low-temperature variation of transmission is linear or constant and the peak below T_c predicted by the BCS theory is not observed. Flat temperature dependence at higher frequencies indicates that the photon energy was sufficient for excitation over the optical gap. The *s-wave* BCS theory is adequate for NbN films but not for the YBCO materials.

I. INTRODUCTION

Far-infrared spectroscopy is an important tool for determining various parameters of superconductors. In the past it served as a direct evidence for an energy gap 2Δ in the electronic excitation spectrum of the superconducting state[1]. The microscopic origin of the gap was clarified by the theory of Bardeen, Cooper and Schrieffer[2] which also successfully explained superconductor properties in the static electromagnetic field such as the Meissner effect. Subsequently, Mattis and Bardeen[3] extended the theory to time-dependent electromagnetic interaction and obtained expressions for real and imaginary parts of the complex conductivity. Furthermore, other authors considered effects of impurities[4,5] and strong coupling[6]. Soon after the discovery of high-temperature superconductivity it became obvious that the BCS-based theories supposing *s-wave* pairing of particles are not suitable for copper oxide materials. It is proposed that the order parameter Δ has d or mixed $s+d$ symmetry[7]. The symmetry of the order parameter inevitably influences also the optical properties. Great attention was paid to analysis of the optical spectra of classical and high-T_c superconductors in the IR and FIR regions[8–10]. The spectra are usually measured at several fixed temperatures using continuous source of radiation. The complementary method presented in this paper is known as *laser thermal spectroscopy*[11]. The FIR photon energies $\hbar\omega$ are fixed and the temperature of the sample is swept through the superconducting transition.

The optical properties of a thin film on plane parallel substrate can be computed from the recurrence relations for reflection and transmission coefficients[12]. If the substrate is wedged the expressions eliminating the interference fringes are more suitable[13]. For simplicity we give here a simple formula for transmission of the superconductor film[1] which neglects the interference in the substrate

$$T_S = \left|1 + \frac{\sigma d Z_0}{n+1}\right|^{-2}. \tag{1}$$

Here σ, d, n, Z_0, are conductivity and thickness of the film, index of refraction of the substrate and impedance of free space, respectively. In the case when $|\sigma d Z_0/(n+1)| \gg 1$ the ratio of the transmission of the film in the superconducting state T_S to the transmission T_N in the normal state with conductivity σ_N is reduced to

$$\frac{T_S}{T_N} = \frac{|\sigma_N|^2}{|\sigma|^2}. \tag{2}$$

At low temperatures, where the real part of conductivity $\sigma_1(T)$ is much smaller than the imaginary part $\sigma_2(T)$, the relative transmission can be expressed in terms of the penetration depth $\lambda(T)$[14]

$$\frac{T_S}{T_N} = \mu_0^2 \omega^2 \lambda^4(T)\, |\sigma_N|^2\,, \tag{3}$$

which is often mentioned in discussion of microwave experiments. It was found that the low-temperature properties of the penetration depth can be used to distinguish between various types of symmetry of the order parameter Δ[7]. The *s-wave* BCS model in the local limit predicts exponential increase of the relative penetration depth with temperature[15]

$$\frac{\lambda(T)-\lambda(0)}{\lambda(0)} = \sqrt{\frac{\pi\Delta}{2kT}}\exp\left(-\frac{\Delta}{kT}\right), \qquad T < 0.5T_c \quad (4)$$

whereas the *d-wave* symmetry is manifested by linear or quadratic temperature variation[7].

The low temperature properties of classical superconductors were experimentally studied mainly at microwave and radio frequencies. The exponential temperature dependence of surface resistance or penetration depth was verified for NbN[16] and other materials[15,17,18]. The FIR transmission of NbN films was fitted well using the Mattis-Bardeen theory[19]. The high-T_c superconductors were investigated also in the far-infrared region but the results are still ambiguous. The temperature variation of the relative penetration depth strongly depends on the quality of sample; it was found to be constant, linear or quadratic[14,20,21].

Near the critical temperature the Mattis-Bardeen theory predicts a sharp peak in transmission at frequencies comparable with the optical gap. Some indistinct maximum just below T_c was already observed in classical superconductors by Perkowitz, who measured the temperature dependence of far infrared transmission of NbN films, one homogenous and one highly granular[19]. The peak in transmission predicted by the theory was observed at a reduced level in the homogeneous sample, but it was absent in the granular material. In homogenous V_3Si, which is a less strongly-coupled superconductor a higher maximum below T_c was seen and better agreement with the same theory was achieved[11]. The presence of the peak in the copper oxide superconductors was not observed yet[22]. It is the aim of this work to compare the temperature dependence of far-infrared transmission of low-T_c and high-T_c superconductor thin films.

II. THEORY

In this section we will briefly describe some significant features of the applied theoretical model. The calculations are based on Zimmermann's expressions for complex conductivity of homogenous and isotropic BCS superconductor with arbitrary purity[5]. Furthermore, the superconductor is supposed to be in the local limit ($\xi_0 \ll \lambda$), which is appropriate for both NbN and YBCO materials.

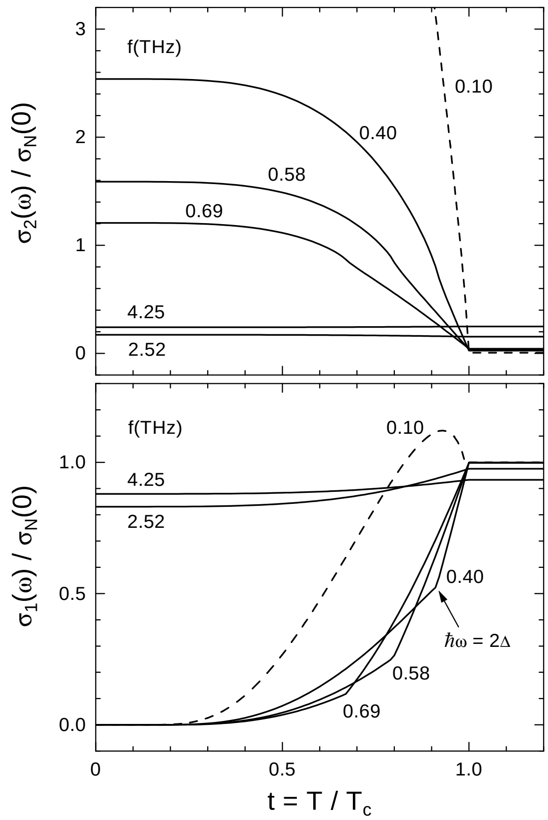

FIG. 1. Theoretical temperature dependence of real and imaginary parts of the BCS complex conductivity. Parameters used in calculation: critical temperature $T_c = 10.8$ K, dc conductivity in the normal state $\sigma_N(0) = 0.45\ \Omega^{-1}\mathrm{m}^{-1}$, electron collision time $\tau = 10^{-14}$ s, optical gap $2\Delta_0 = 3.53\ kT_c$.

The theoretical temperature dependence of the complex conductivity is displayed in fig. 1 for several frequencies in the range of interest and parameters relevant to NbN listed below the figure. Real and imaginary parts of conductivity are almost temperature independent for photon energies above the optical gap ($\hbar\omega \gg 2\Delta_0$). For photon energy comparable with the gap ($\hbar\omega \approx 2\Delta_0$) the temperature behavior can be understood in the framework of the simple *two-fluid model*: Below T_c the imaginary part increases with decreasing temperature and the real part declines to zero. At temperature T_ω for which photon energy coincides with the gap $\hbar\omega = 2\Delta(T_\omega)$ a discontinuity of slope appears on the σ_1 curves. At low enough frequencies ($\hbar\omega \ll 2\Delta_0$) a "coherence peak" arises in the real part of conductivity[23] (dashed line).

The complex conductivity $\sigma = \sigma_1 + i\sigma_2$ presented in the previous paragraph is used to calculate the optical properties of a free standing thin film. From the relative complex permitivity $\epsilon_r = \epsilon_\infty + i\sigma/\omega$ we get the complex index of refraction which enters the Airy's formulas for reflection and transmission coefficients[12]. Computed optical parameters are displayed in fig. 2.

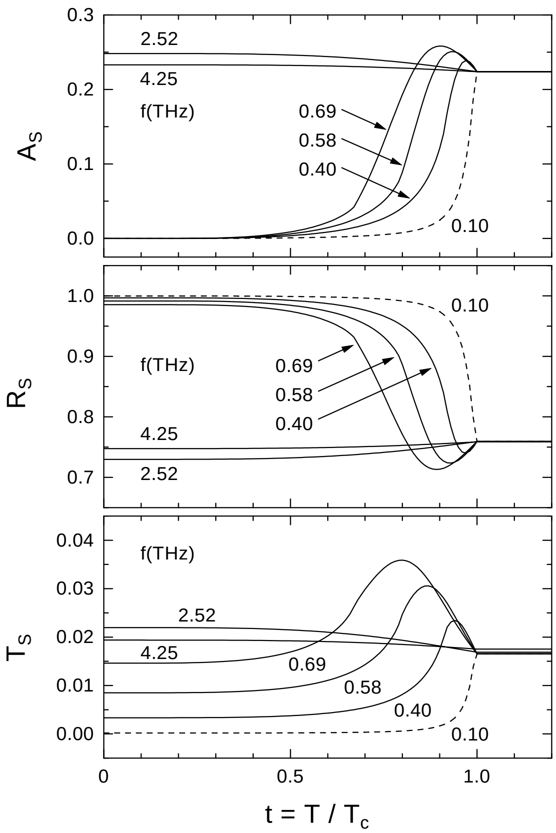

FIG. 2. Optical properties of a free standing superconductor film: transmission T_S, reflection R_S and absorption A_S. Material parameters same as in fig. 1, film thickness $d_{\rm film} = 80$ nm, $\epsilon_\infty = 0$.

In the high frequency limit, $\hbar\omega \gg 2\Delta_0$, the optical properties exhibit only flat, almost linear temperature dependence, not much different from the normal state. In the low frequency limit, $\hbar\omega \ll 2\Delta_0$, the optical parameters change from the normal state values with decreasing temperature. Transmission and absorption fall monotonously to zero whereas reflection comes to 100% at zero temperature. At frequencies slightly lower then gap, $\hbar\omega \tilde{<} 2\Delta_0$, a maximum appears in transmission and absorption just below T_c, while reflection exhibits a minimum. The peak in the optical properties does not correspond to the low frequency coherence peak in the real part of conductivity. Even monotonous dependence of the real and imaginary parts of conductivity may result in a peak in the optical properties if the real part of conductivity decreases more quickly than the imaginary part increases.

III. EXPERIMENT

The temperature dependence of FIR transmission was studied on two classical superconductor samples and two copper oxide samples. A high quality epitaxial NbN film (A) was deposited on MgO substrate and a polycrystalline NbN thin film (B) on Si substrate. A $YBa_2Cu_3O_{7-\delta}$ thin film (C) was prepared from a stoichiometric target by magnetron diode sputtering on MgO polished substrate oriented in the (100) plane. The c-axis of the grown film was directed perpendicularly to the sample plane. In order to eliminate light interference the substrate was slightly wedged. Another $YBa_2Cu_3O_{7-\delta}$ film (D) was deposited on sapphire substrate covered by a very thin CeO_2 buffer layer. The substrate was slightly wedged to suppress interference effect. Experimental parameters of the measured samples are summarized in Table 1.

The results presented in this paper were obtained mostly using the far infrared laser based spectrophotometer[24] in the Institute of Physics in Prague except for the measurements on the high quality NbN film (A) which were performed on a similar equipment[10] in the National Research Laboratory of Metrology in Tsukuba. We will briefly describe the former experimental set-up (for details see[24]). The source of the FIR radiation is an optically pumped gas laser which emits linearly polarised light at discrete frequencies in the range from 0.4 up to 4.3 THz (13-140 cm^{-1}, 1.7-18 meV, 742-70 μm). Stability of the output laser power is monitored by a pyroelectric detector and the radiation transmitted through the sample is detected by a silicon bolometer kept at the working temperature of 1.7 K. Transmission is proportional to the ratio of the signals from the bolometer and from the pyroelectric detector. As proved by careful testing, the sample holder is free of optical leakage. Background radiation is suppressed by an IR low pass filter inserted before the sample. Temperature of the sample can be controlled continuously in the range 4.2 - 130 K and it is measured by a GaAs diode sensor attached to the sample holder. A small amount of helium exchange gas admitted into the sample space ensures good thermal contact. To enable correction of little difference between the sample and sensor temperatures the ac susceptibility at 330 Hz was monitored simultaneously with the transmission experiments. By this method the true superconducting phase transition is determined independently and the temperature axis rescaled accordingly.

TABLE I. Parameters $d_{\rm film}$, T_c, ρ_N listed in the table represent the film thickness, the critical temperature, the dc resistivity in the normal state just above T_c. The substrates are in the shape of plate or wedge with dimensions $10 \times 10 \times d_{\rm sub}$ mm^3 where the thickness $d_{\rm sub}$ or the extent of the wedge is given in the last column.

Sample	Film	$d_{\rm film}$ [nm]	T_c [K]	ρ_N [$\mu\Omega$cm]	Substrate/ Buffer layer	$d_{\rm sub}$ [mm]
A	NbN	410	14.7	71	MgO	0.50
B	NbN	70-90	10.8	220	Si/SiO_2	0.25
C	YBCO	200-220	89	?	MgO	0.37-0.98
D	YBCO	120-140	87	100	Al_2O_3/CeO_2	0.36-0.67

IV. RESULTS

The experimental results are presented in figures 3-7 together with the theoretical estimates. The temperature dependence of the relative transmission T_S/T_N is plotted in the reduced temperature scale $t = T/T_c$. The intensity transmitted through the sample is normalized to that in the normal state taken at a temperature slightly above the superconducting transition.

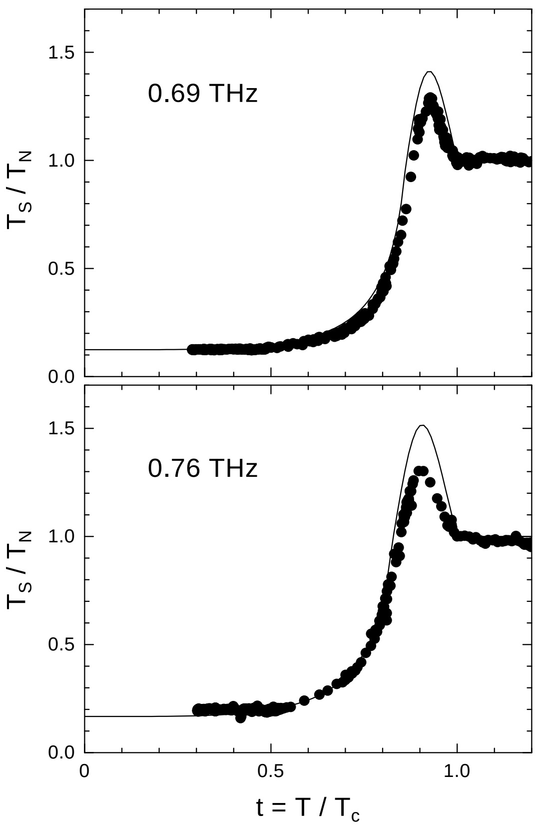

FIG. 3. Temperature dependence of the relative transmission of NbN film A - experiment (points) and theory (lines). Parameters used in calculation: critical temperature $T_c = 14.7$ K, dc conductivity in the normal state $\sigma_N(0) = 1.4 \times 10^6\ \Omega^{-1}\ \mathrm{m}^{-1}$, electron collision time $\tau = 0.5 \times 10^{-14}$ s, optical gap $2\Delta_0 = 3.53\ kT_c$, film thickness $d_{\rm film} = 410$ nm, substrate thickness $d_S = 0.5$ mm, index of refraction of the substrate $n_{\rm sub} = 4.85 + 1.5 \times 10^{-7} i$.

The measurements performed on the high quality NbN film (A) at laser frequencies 0.69 and 0.76 THz are shown in fig. 3. The transmission peak just below T_c is sharp and well pronounced. At very low temperatures the shape of the dependence was not reliably resolved, as due to the relatively high film thickness the transmitted power was small.

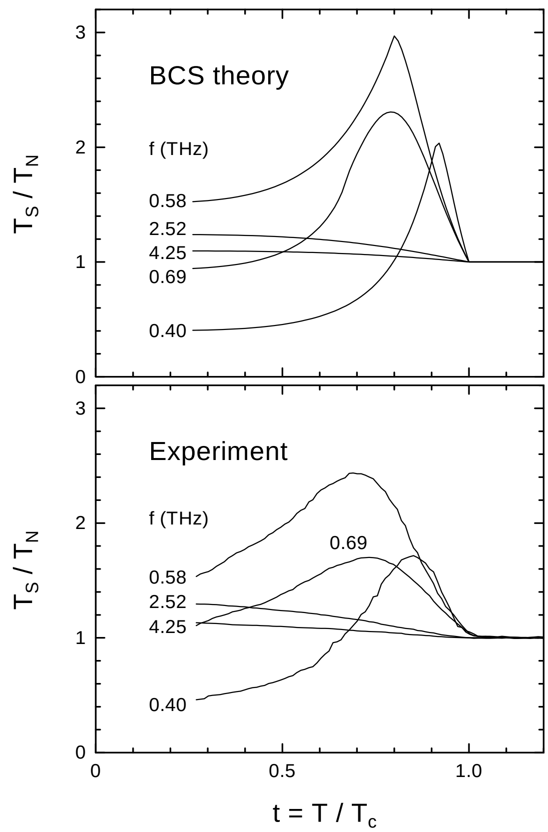

FIG. 4. Temperature dependence of the relative transmission of NbN thin film B - experimental and theoretical. Parameters used in calculation: critical temperature $T_c = 10.8$ K, dc conductivity in the normal state $\sigma_N(0) = 0.45 \times 10^6\ \Omega^{-1}\mathrm{m}^{-1}$, electron collision time $\tau = 10^{-14}$ s, optical gap $2\Delta_0 = 3.53\ kTc$, film thickness $d_{\rm film} = 80$ nm, substrate thickness $d_{\rm sub} = 0.25$ mm, index of refraction of the substrate $n_{\rm sub} = 3.5$.

The polycrystalline NbN thin film (B) exhibits a broad peak near T_c at laser frequencies 0.4, 0.58 and 0.69 THz but a flat dependence at frequencies 2.52 and 4.25 THz (see fig. 4). The relative penetration depth displayed in fig. 5 was calculated from the low temperature measurement at frequency 0.4 THz. The experimental data were fitted using the exponential expression (4) which follows from the BCS theory.

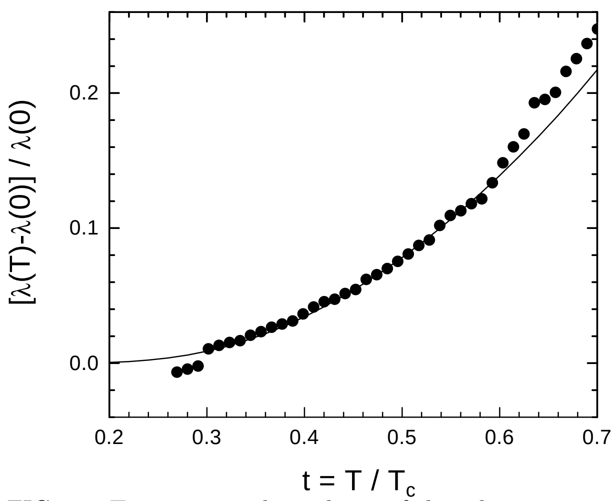

FIG. 5. Temperature dependence of the relative penetration depth of NbN thin film B - experiment (points) and the best fit (line) with the gap value $2\Delta_0 = 3.53\ kT_c$.

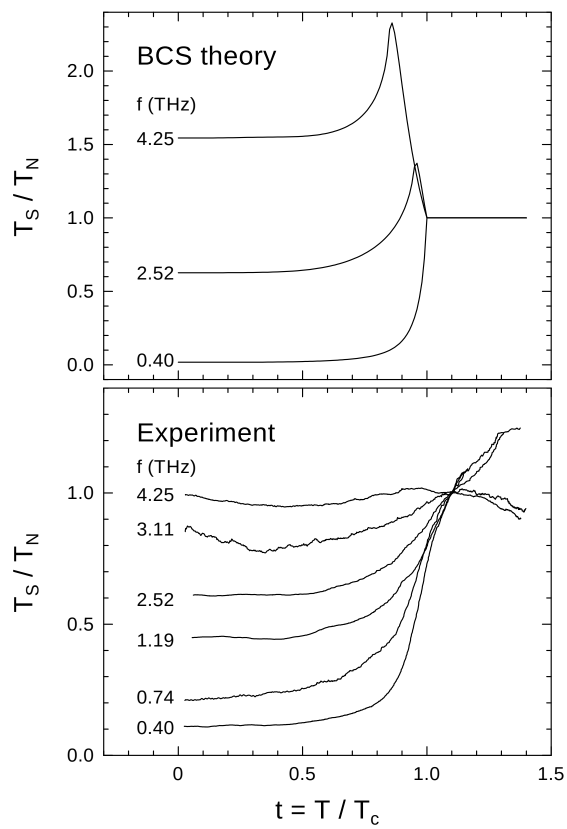

FIG. 6. Temperature dependence of the relative transmission of $YBa_2Cu_3O_{7-\delta}$ thin film C - measured and calculated from the BCS theory with parameters: $T_c = 89\ K$, dc conductivity in the normal state $\sigma_N(0) = 10^6\ \Omega^{-1}\mathrm{m}^{-1}$, electron collision time $\tau = 3.5 \times 10^{-14}$ s, optical gap $2\Delta_0 = 3.53\ kT_c$, film thickness $d_{\mathrm{film}} = 210$ nm, substrate thickness $d_{\mathrm{sub}} = 0.5$ mm, index of refraction of the substrate $n_{\mathrm{sub}} = 4.85 + i\ 1.5 \times 10^{-7}$.

At low temperatures the transmission of the YBCO sample (C) changes slightly or is almost constant (see fig. 6). At the vicinity of T_c a clear step appears in transmission for lower frequencies 0.40-2.5 THz. The magnitude of the step diminishes towards higher frequencies and above 3.11 THz the dependence on temperature becomes nearly flat. The sharp peak expected by the BCS theory is absent. Similarly for the YBCO film (D) the transmission grows monotonously up to T_c without any maximum (see fig. 7).

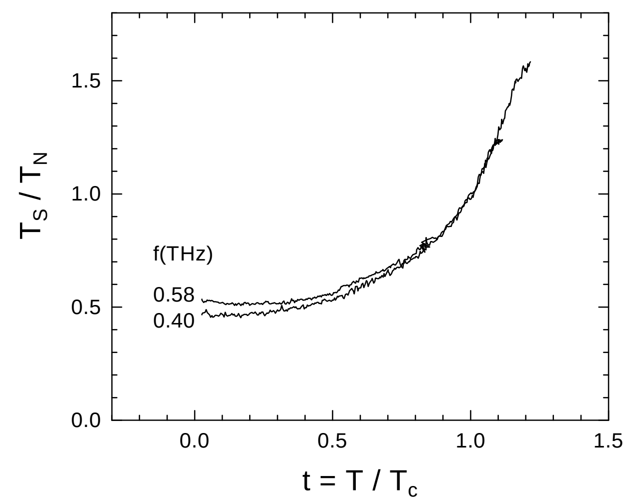

FIG. 7. Temperature dependence of the relative transmission of $YBa_2Cu_3O_{7-\delta}$ thin film D.

The theoretical curves are calculated with parameters listed in the figure captions. In particular the experimental data from table 1 are exploited, the gap is fixed at the BCS value $2\Delta_0 = 3.53\ kT_c$, for electron collision time τ a reasonable guess is used. High frequency permitivity ϵ_∞ is neglected and the index of refraction of the substrate n_{sub} is taken from the literature. In the theoretical estimates of the FIR transmission of the NbN samples (A,B) also the multiple reflections in the substrate are included[12]. Interference of the FIR radiation affected qualitatively only the transmission of the NbN sample B (fig. 4), for which an irregularity in the curve ordering should be noticed. For both YBCO samples (C,D) which are deposited on wedged substrates the formula neglecting intererence effect was used[13].

V. CONCLUSIONS

In the theoretical model the following feature was observed for the range of applied parameters: if the real part of conductivity exhibits a maximum below T_c the optical parameters change monotonously with temperature and vice versa.

The temperature dependence of the far-infrared relative transmission of classical and high-temperature superconductor films is substantially different. The NbN experimental data are well described by calculations based on the *s-wave* BCS model. In the NbN samples,

the exponential increase of relative penetration depth at low temperatures and the peak in transmission near T_c at frequencies below the optical gap were observed. The peak strongly depends on the quality of the sample. In the high quality sample (A) it corresponds well to BCS calculations, whereas in the polycrystalline sample (B) the observed maximum is somewhat broader and its level a little lower than theoretical. This behavior is in accordance with other experiments which were performed on granular films[19]. In the YBCO samples, the low temperature variation of transmission is non-measurably small and the peak below T_c predicted by the BCS theory is missing. The flat temperature dependence at laser frequency 4.3 THz (fig. 6) indicates that the photon energy was sufficient for excitation over the optical gap. The *s-wave* BCS theory is adequate for NbN films but it is not appropriate for the YBCO materials.

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